

# THEORY OF LUMINESCENT EMISSION IN NANOCRYSTAL ZnS:Mn WITH AN EXTRA ELECTRON

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(February 6, 2008)

## Abstract

We consider the effect of an extra electron in a doped quantum dot  $ZnS : Mn^{2+}$ . The Coulomb interaction and exchange interaction between the extra electron and the states of the Mn ion will mix the wavefunctions, split the impurity energy levels, break the previous selection rules and change the transition probabilities. Using this model of an extra electron in the doped quantum dot, we calculate the energy and the wave functions, the luminescence efficiency and the transition lifetime and compare with the experiments. Our calculation shows that two orders of magnitude of lifetime shortening can occur in the transition  $^4T_1 - ^6A_1$ , when an extra electron is present.

PACS numbers: 73.20.Dx, 78.60.J, 42.65, 71.35

## I.Introduction.

In contrast to undoped materials, the impurity states in a doped nanocrystal play an important role in the electronic structure, transition probabilities and the optical properties. In recent years, attempts to understand more about these zero-dimensional nanocrystal effects have been made in several labs by doping an impurity in a nanocrystal, searching for novel materials and new properties, and among them Mn-doped ZnS nanoparticles have been intensively studied [1-15]. Among many bulk wide band gap compounds, manganese is well known as an activator for photoluminescence (PL) and electroluminescence (EL) and the  $Mn^{2+}$  ion d-electrons states act as efficient luminescent centers while doped into a semiconductors.

In 1994 Bhargava and Gallagher[1, 2] reported the first realization of a ZnS semiconductor nanocrystal doped with Mn isoelectronic impurities and claimed that Mn-doped ZnS nanocrystal can yield both high luminescence efficiency and significant lifetime shortening. The yellow emission characterized for  $Mn^{2+}$  in bulk ZnS [16-18], which is associated with the transition  $^4T_1 - ^6A_1$ , was reported to be observed in photoluminescence (PL) spectra for the  $Mn^{2+}$  in nanocrystal ZnS. In nanocrystals, however, the PL peak for the yellow emission is reported slightly shifted toward a lower energy (in bulk ZnS:Mn it peaks around 2.12 eV, in nanocrystal ZnS:Mn it peaks at 2.10 eV). Also, the reported linewidth of the yellow emission in the PL spectrum for a nanocrystal is larger than for the bulk. Most strikingly, the luminescence lifetime of the  $Mn^{2+} \ ^4T_1 - ^6A_1$  transition was reported to decrease by 5 orders of magnitude, from 1.8 ms in bulk to 3.7 ns and 20.5 ns in nanocrystals while maintaining the high (18%) quantum efficiency.

In ref. [6] the authors suggested that the increase in quantum efficiency as well as the lifetime shortening is the result of strong hybridization of s-p electrons of the ZnS host and d- electrons of the Mn impurity due to confinement, and also of the modification of the crystal field near the surface of the nanocrystals. Stimulated by this dramatic result, many other laboratories are trying to synthesize the Mn-doped ZnS nanocrystals and considerable attention has been paid to optical properties of these kind of materials[7-13]. Yu et al.[8] reported obtaining the yellow emission peak of  $^4T_1 - ^6A_1$ , the slight shift of the peak toward the high energy and the increase in luminescence efficiency. Sooklai et al. [9] reported the shortening of the decay time to ns for nanocrystals  $ZnS : Mn^{2+}$  while Ito et al. [10] obtained the life time shortening to  $\mu s$  in  $ZnTe : Mn^{2+}$  quantum well. Very recently, D. Norris et al.[13] reported obtaining high quality ZnSe colloidal nanocrystals doped with single  $Mn^{2+}$  impurities. Also, several different groups have proposed models to try to explain the processes occurring with the impurity centers inside the confined nanocrystals [6,14-15]. But while it is now well established that the confinement effect strongly modifies the electronic structure of nanocrystals, the effects of the confinement on the energy structure and transitions of the Mn impurity in the nanocrystals, still are controversial. Also, there might exist different mechanisms to change the optical processes for doping centers in nanocrystals.

Here we investigate a new effect and mechanism to study Mn doping in a nanocrystal. Our model is to assume there is an extra electron in a doped dot. The electron may originate in the dot itself, or might be injected into the dot. The extra electron will strongly couple to the electron involved in the transitions, split the energy levels and mix the wavefunctions, and will thus break the former selection rules. Because the dot is small, the boundary conditions enhance the coupling, so by controlling the presence or absence of the extra

electron in the dot, one can control the optical transitions in the dot. This can provide the explanation for the observed shortening of lifetime and enhancement of the quantum efficiency.

The transition of our interest here is  $^4T_1 - ^6A_1$  of the  $Mn^{2+}$  ion in the crystal field of the ZnS nanocrystal. The luminescent transition from the lowest excited level  $^4T_1$  (spin  $\frac{3}{2}$ ) to the ground state (spin  $\frac{5}{2}$ ) is spin-forbidden. But, the weak spin-orbital interaction makes the transition slightly allowed [16-18].

Actually, for the Mn-center we have a configuration of  $d^5$  electrons. If we consider the ways in which transitions can take place between the energy levels of a  $d^n$  center, we find that the electric dipole transitions are forbidden due to parity ( all the d-states are of even parity). But for the crystal field whose symmetry group does not contain the inversion symmetry, which is our case (local symmetry is  $C_{3v}$  in the wurtzite symmetry of ZnS), the electric dipole transition becomes possible due to the mixing of odd-parity states into the  $d^n$  states, which means the wavefunctions of the Mn-center states now contains both the parities [19-20]. Meanwhile, a small fraction of the 4p atomic orbitals is likely mixed into the 3d-orbital and the typical states are written in the form:

$$\Psi^i(3d^n) = \Psi_0^i(3d^n) + \beta\chi^i(4p) \quad (1)$$

where  $\Psi_0^i(3d^n)$  is the i-state even parity wavefunction of the  $d^5$  electron and  $\chi^i(4p)$  is the odd parity wavefunction of the 4p electron.  $\beta$  is a small coefficient. Then the electric dipole transitions between the i-state and j-state, for example, of the doping center can arise due to non-zero matrix elements between  $\Psi_0^i(3d^n)$  and  $e\chi^j(4p)$  and between  $e\chi^i(4p)$  and  $\Psi_0^j(3d^n)$  even though the matrix elements between  $\Psi_0^i(3d^n)$  and  $\Psi_0^j(3d^n)$  are zeros.

Due to this unsymmetrical environment the electric dipole transition between the ground state  $^6A_1$  and the first excited state  $^4T_1$  is orbitally possible. But due to spin difference the transition is spin-forbidden. This rule is slightly relaxed due to the spin-orbit interaction. But because the spin-orbit interaction is very weak, the oscillator strength is very small, which leads to the luminescence life time of ms order of magnitude. In order for the transition to be allowed, there must be some mixing that breaks the spin selection rules.

If an extra electron is in the dot, the electron will couple with the electrons of  $Mn^{2+}$  in each state, namely the electron will couple with the states  $^4T_1$  and  $^6A_1$ . The coupling will mix different states and will produce the states with the same spin, between which the electric dipole will be allowed.

In this work we consider as the coupling hamiltonian the Coulomb and Exchange interactions. The perturbed wavefunctions of the  $d^5$  electrons in  $^6A_1$  and  $^4T_1$  states will be derived in the next two sections. For the extra electron which is confined in the dot and localized at some lattice point, we will use the Wannier exciton function:

$$\Psi_{1S}^{Dot}(r) = \sum_{a_i} \varphi_{1S}^{Dot}(r) w_{a_i}(r - a_i) \quad (2)$$

here  $w_{a_i}(r - a_i)$  is the Wannier function of the exciton localized at the lattice point  $a_i$ , where  $a_i$  is the distance from the origin to the lattice point i inside the dot.  $\varphi_{1S}^{Dot}(r)$  is the envelope function for a confined electron in the sphere:

$$\varphi_{(1s)}^{Dot} = R_{1s}^{Dot} Y_0^0 | \frac{1}{2}, \sigma > \quad (3)$$

where  $Y_0^0$  is a spherical harmonics,  $| \frac{1}{2}, \sigma \rangle$  is the spin function for the electron with spin  $s = \frac{1}{2}$  and  $\sigma = +$  or  $-$  for spin up and spin down states.  $R_{1s}^{Dot}$  is the envelope function for the  $1S$  electron confined in a sphere of radius R (2.4)

$$R_{nl}^{Dot}(r) = \sqrt{\frac{2}{R^3}} \frac{j_l(\chi_{nl} \frac{r}{R})}{j_{l+1}(\chi_{nl})} \quad (4)$$

where  $j_{nl}$  is the spherical Bessel function,  $\chi_{nl}$  is the location of the zero of the spherical Bessel function.

The interaction Hamiltonian between the extra electron and the  $d^5$  electrons is given in section III. In section II we will derive the wavefunctions for the  $d^5$  electrons in  $^4T_1$  and  $^6A_1$  states using the strong limit field approximation.

## II. $3d^5$ Electron in the Crystal Field -Crystal Field. Manganese Energy Levels and Wavefunctions

Impurity centers are formed by foreign ions substituting for host ions or placed interstitially in the lattice. When the activator ions such as Mn are placed in the crystal field of the semiconductor lattice, the crystal field would affect the wavefunctions and energy structure of the impurity to form "crystal field states" of the impurity ions. For the transition metal ions with the outer  $3d^n$  electron configuration, the crystal field energy and the interelectron Coulomb interaction are comparable[18,19], so these  $d^n$  electrons can be treated either in the intermediate crystal field or in the strong crystal field limit, and they are more often treated in the strong field approximation. Then the fivefold degenerate 3d level will split principally into two levels, the two-fold degenerate level with the additional energy  $+6Dq$ , and the three-fold degenerate one with the additional energy of  $-4Dq$ . Here  $Dq$  is a single parameter which characterizes the strength of an octahedral crystal field [19,20]. In Fig. 1 the splitting diagram for a 3d electron in the octahedral crystal field is shown[19]. In this section we will derive the wavefunctions of the  $d^5$  electrons of the Mn impurity in the crystal field. We note that it is customary in this system to treat the local site symmetry as octahedral for the major  $t_2 - e$  splitting and then add a small axial field to reduce the site symmetry to the  $C_{3V}$  of wurtzite structure.

The eigenstates of the two-fold degenerate level (the e-orbitals) are written in the following form (see eqn (1) above for prototype):

$$\begin{aligned} \phi_{eu} &= |3d0\rangle = R_{3d}(r)\left(\frac{5}{4\pi}\right)^{1/2}\left(\frac{3z^2 - r^2}{2r^2}\right), \\ \phi_{ev} &= \left(\frac{1}{2}\right)^{1/2}(|3d2\rangle + |3d-2\rangle) = R_{3d}(r)\left(\frac{5}{4\pi}\right)^{1/2}3^{1/2}\left(\frac{x^2 - y^2}{2r^2}\right) \end{aligned} \quad (5)$$

And the eigenstates for the three-fold degenerate level (the  $t_2$ -orbital) are written as:

$$\begin{aligned} \phi_{t_2\xi} &= \left(\frac{i}{2}\right)^{1/2}(|3d1\rangle + |3d-1\rangle) = R_{3d}(r)\left(\frac{5}{4\pi}\right)^{1/2}3^{1/2}\left(\frac{yz}{r^2}\right), \\ \phi_{t_2\eta} &= -\left(\frac{1}{2}\right)^{1/2}(|3d1\rangle - |3d-1\rangle) = R_{3d}(r)\left(\frac{5}{4\pi}\right)^{1/2}3^{1/2}\left(\frac{xz}{r^2}\right), \\ \phi_{t_2\zeta} &= -\left(\frac{i}{2}\right)^{1/2}(|3d2\rangle - |3d-2\rangle) = R_{3d}(r)\left(\frac{5}{4\pi}\right)^{1/2}3^{1/2}\left(\frac{xy}{2r^2}\right) \end{aligned} \quad (6)$$

For simplicity, from now on we will denote these double degenerate and triple degenerate eigenstates  $u, v$  and  $\xi, \eta, \zeta$ , respectively.

For a multi-3d-electron system, the orbital Hamiltonian in crystal field will be the following:

$$H = \sum_i H_0^0(r_i) + \sum_{i>j} H'(r_i, r_j) \quad (7)$$

where  $H_0^0(r_i)$  is the Hamiltonian of a single electron interacting with crystal field,  $H'(r_i, r_j)$  is the electron-electron interaction Hamiltonian between the d-electrons. For the strong crystal field limit, the Hamiltonian  $H_0^0(r_i)$  will be solved first to obtain the wavefunctions of a single 3d electron as in the last chapter, then these states will be interacting by the Hamiltonian  $H'(r_i, r_j)$ . The wavefunctions of 3d-electron orbitals are  $u, v$ , which belong to the E irreducible representation, and  $\xi, \eta, \zeta$  which belong to the  $T_2$  reducible representation. So in the strong crystal field case, the wavefunctions of multi-3d-electron Hamiltonian will be the products of these one-electron orbitals.

In an octahedral crystal field, the Hamiltonian (5) is invariant under all the rotation operators of the group  $O_h$ , where for the first term the rotations are applied independently for each  $r_i$  and for the second term the rotations are applied simultaneously for all  $r_i$ . Then the wavefunctions will transform according to irreducible representation of the  $O_h$  group.

Begining the reduction process for the two 3d electrons configuration, we will have the products  $E \times E, T_2 \times T_2$  and  $T_2 \times T_2$  [19,20]. The  $E \times E$  product functions will belong to  $A_1, A_2$  and E irreducible representation. We will denote as  $|e^2, A_1\rangle$  the function of the product  $E \times E$  which belongs to the  $A_1$  representation. The  $|e^2, A_1\rangle$  function is symmetric under interchange of  $r_1, r_2$ . Then because of the Pauli principle, to obtain the antisymmetric total function its spin function must be the antisymmetric spin function with the total spin  $S=0$

$$|S = 0, M_S = 0\rangle = \frac{1}{\sqrt{2}} [\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)] \quad (8)$$

where  $\alpha(\sigma)$  and  $\beta(\sigma)$  are the up ( $|\uparrow\rangle$ ) and down ( $|\downarrow\rangle$ ) spin functions. If one use the wavefunction  $[u^+ u^-]$  to denote the normalized two by two Slater determinant of the products of the orbital and the spin functions  $u(r_i)\alpha(\sigma_j)$  where  $i, j = 1, 2$  then the final full wavefunction  $|e^2, A_1\rangle$  is written in the short form

$$|e^2, A_1, M_S = 0\rangle = \frac{1}{\sqrt{2}} ([u^+ u^-] + [v^+ v^-]) \quad (9)$$

Similarly for the wavefunctions  $|e^2, A_2\rangle$  of the  $E \times E$  orbitals which belongs to  $A_2$  representation we have the antisymmetric orbital wavefunction, then the spin functions must be three symmetric spin functions of the total spin  $S=1$ . Denoting the spin index  $2S + 1$  on the left of the representation  $A_2$  we write the total wavefunctions of  $|e^2, A_2\rangle$  in the form:

$$\begin{aligned} |e^2, {}^3A_2, M_S = 1\rangle &= |u^+ v^+| \\ |e^2, {}^3A_2, M_S = 0\rangle &= ([u^+ v^-] + [u^- v^+]) \\ |e^2, {}^3A_2, M_S = -1\rangle &= [u^- v^-] \end{aligned} \quad (10)$$

and for the  $|e^2, E >$  wavefunctions one gets:

$$\begin{aligned} |e^2, {}^1 Eu, M_S = 0 > &= \frac{1}{\sqrt{2}} ([u^+ u^-] - [v^+ v^-]) \\ |e^2, {}^1 Ev, M_S = 0 > &= \frac{1}{\sqrt{2}} ([u^+ v^-] - [u^- v^+]) \end{aligned} \quad (11)$$

Continuing in this way one can get all the possible wavefunctions and energies for  $t^n, e^n$  and  $t^m e^k$  configuration of  $3d^n$  in the octahedral crystal field [20]. The ground state of the  $3d^5$  configuration is the sextet  ${}^6 A_1$  with the total spin  $\frac{5}{2}$ . The first excited level is the triplet states  ${}^4 T_1$ , which is the excited state closest to the ground state. We are interested in the optical transition between the first excited state and the ground state, this is the transition  ${}^4 T_1 - {}^6 A_1$ . The wavefunction of  ${}^6 A_1$  and  ${}^4 T_1$  states can be derived, using the table of coupling coefficients from [20,21,23].

The ground state - the sextet  ${}^6 A_1$  is derived from  $t_2^3 \times e^2$ . From the table [21] the  ${}^6 A_1$  state is:

$$\begin{aligned} |{}^6 A_1 > &= |t_2^3({}^4 A_2)e^2({}^3 A_2), {}^6 A_1 a_1\rangle \\ &= |t_2^3({}^4 A_2)\rangle |e^2({}^3 A_2)\rangle \end{aligned} \quad (12)$$

The functions of  $t_2^3({}^4 A_2)$  and  $E^2({}^3 A_2)$  are [21]:

$$\begin{aligned} |t_2^3({}^4 A_2)\frac{3}{2}a_2 > &= [-\xi^+ \eta^+ \zeta^+] \\ |e^2({}^3 A_2)1a_2 > &= [u^+ v^+] \end{aligned} \quad (13)$$

Then we have for the wavefunctions of the ground state  ${}^6 A_1$ :

$$|{}^6 A_1 a_1 > = [-\xi^+ \eta^+ \zeta^+ u^+ v^+] \quad (14)$$

The triplet  ${}^4 T_1$  wavefunctions of  $3d^5$  are derived from  $t_2^4({}^3 T_1) \times e^1({}^2 E)$ .

$$\begin{aligned} |{}^4 T_1(3d^5)\frac{3}{2}x > &= |t_2^4({}^3 T_1)e^1({}^2 E), {}^4 T_1\frac{3}{2}x\rangle \\ |{}^4 T_1(3d^5)\frac{3}{2}y > &= |t_2^4({}^3 T_1)e^1({}^2 E), {}^4 T_1\frac{3}{2}y\rangle \\ |{}^4 T_1(3d^5)\frac{3}{2}z > &= |t_2^4({}^3 T_1)e^1({}^2 E), {}^4 T_1\frac{3}{2}z\rangle \end{aligned} \quad (15)$$

and we obtained the wavefunctions of the triplet  ${}^4 T_1$  of the  $d^5$  configuration in the octahedral crystal field:

$$\begin{aligned} |{}^4 T_1(3d^5)\frac{3}{2}x > &= -\frac{1}{2}[\xi^+ \xi^- \eta^+ \zeta^+ u^+] - \frac{\sqrt{3}}{2}[\xi^+ \xi^- \eta^+ \zeta^+ v^+] \\ |{}^4 T_1(3d^5)\frac{3}{2}y > &= \frac{1}{2}[\xi^+ \eta^+ \eta^- \zeta^+ u^+] + \frac{\sqrt{3}}{2}[\xi^+ \eta^+ \eta^- \zeta^+ v^+] \\ |{}^4 T_1(3d^5)\frac{3}{2}z > &= [\xi^+ \eta^+ \zeta^+ \zeta^- u^+] \end{aligned} \quad (16)$$

We recall here that the wavefunctions in (14) and (16) are five by five Slater determinants which we have written in the short notation.

As discussed before, in the actual relevant  $C_{3V}$  crystal field ZnS:Mn with no inversion symmetry, the  $4p$ -states with odd parity can be mixed into the  $3d^5$  state with even parity. Consider the configuration of the  $3d^5$  electrons of the Mn- center with the  ${}^6A_1$  being the ground state and  ${}^4T_1$  as the first excited state. We can assume that because the  ${}^6A_1$  level is the ground state, it can be considered to be far away from other states, including the  $4p$  state. So we can consider the  ${}^6A_1$  as a  $3d^5$  -pure state. Since the  ${}^4T_1$  is the excited state, it will be closer in energy to other  $4p$  state and the probability that it will be mixed with the odd-parity states will be much higher. The p electron has the  $t_1$  wavefunction. From the configuration of  $3d^5$  electrons, we see that the  ${}^4T_1$  state arose from  $t_2^4({}^3T_1) \times e^1({}^2E)$ . Because of symmetry, it is reasonable to assume that the state  $|3d^5\{{}^4T_1(t_2^4 \times e^1)\}\rangle$  is more likely to mix with the configuration  $|3d^44p\{{}^4T_1(t_2^4 \times t^1)\}\rangle$ . Or we can say that the configuration with four d-electrons in the function  $t_2$  and one electron in function e is more likely to mix with the configuration with only a little energy difference, which also has 4 d-electrons in the same functions  $t_2$  and only the fifth electron being the  $t_1$  function instead of the e-function as in other configuration.

Now consider the configuration  $|3d^44p\{t_2^4 \times t^1\}\rangle$ . The  $t_2^4$  configuration is a combination of  ${}^1A_1 + {}^1E + {}^3T_1 + {}^1T_2$ . The product of all these four functions with the function  ${}^2T_1$  of the p-electron can give the triplet  $T_1$ , but among those states only the product of  ${}^3T_1$  with  ${}^2T_1$  can give the exact spin of the state  ${}^4T_1$ . Then we have the only odd state which can mix with our  $|3d^5\{{}^4T_1[t_2^4({}^3T_1) \times e^1({}^2E)]\}\rangle$  state is the state  $|3d^44p\{{}^4T_1(t_2^4({}^3T_1) \times t^1({}^2T_1))\}\rangle$ .

Recalling the eigenstates of the p-electron:

$$\begin{aligned} |p_z\rangle &= |2P0\rangle = -iR_{20}|Y_{10}\rangle, \\ |p_x\rangle &= \frac{i}{\sqrt{2}}(|2P1\rangle - |2P-1\rangle) = \frac{i}{\sqrt{2}}R_{20}(|Y_{11}\rangle - |Y_{11}\rangle), \\ |p_x\rangle &= \frac{1}{\sqrt{2}}(|2P1\rangle + |2P-1\rangle) = \frac{i}{\sqrt{2}}R_{20}(|Y_{11}\rangle + |Y_{11}\rangle) \end{aligned} \tag{17}$$

we obtain the triplet  ${}^4T_1$  of the  $d^4p$  configuration in the crystal field:

$$\begin{aligned} |{}^4T_1(3d^44p)x\rangle &= \frac{1}{\sqrt{2}}[\xi^+\eta^2\zeta^+p_z^+] - \frac{1}{\sqrt{2}}[\xi^+\eta^+\zeta^2p_y^+] \\ |{}^4T_1(3d^44p)y\rangle &= \frac{1}{\sqrt{2}}[\xi^2\eta^+\zeta^+p_z^+] - \frac{1}{\sqrt{2}}[\xi^+\eta^+\zeta^2p_x^+] \\ |{}^4T_1(3d^44p)z\rangle &= -\frac{1}{\sqrt{2}}[\xi^2\eta^+\zeta^+p_y^+] - \frac{1}{\sqrt{2}}[\xi^+\eta^2\zeta^+p_x^+] \end{aligned} \tag{18}$$

And finally we have the wavefunctions of the triplet  ${}^4T_1$  of the Mn-center:

$$\begin{aligned} |{}^4T_1x\rangle &= -\frac{1}{2}[\xi^+\xi^-\eta^+\zeta^+u^+] - \frac{\sqrt{3}}{2}[\xi^+\xi^-\eta^+\zeta^+v^+] + \frac{\beta}{\sqrt{2}}[\xi^+\eta^2\zeta^+p_z^+] - \frac{\beta}{\sqrt{2}}[\xi^+\eta^+\zeta^2p_y^+] \\ |{}^4T_1y\rangle &= \frac{1}{2}[\xi^+\eta^+\eta^-\zeta^+u^+] + \frac{\sqrt{3}}{2}[\xi^+\eta^+\eta^-\zeta^+v^+] + \frac{\beta}{\sqrt{2}}[\xi^2\eta^+\zeta^+p_z^+] - \frac{\beta}{\sqrt{2}}[\xi^+\eta^+\zeta^2p_x^+] \\ |{}^4T_1(3d^5)\frac{3}{2}z\rangle &= [\xi^+\eta^+\zeta^+\zeta^-u^+] - \frac{\beta}{\sqrt{2}}[\xi^2\eta^+\zeta^+p_y^+] - \frac{\beta}{\sqrt{2}}[\xi^+\eta^2\zeta^+p_x^+] \end{aligned} \tag{19}$$

### III. The Coulomb and Exchange Interaction

The Coulomb and Exchange interaction will couple the extra electron and the impurity electrons and then result in different spin configurations, so we expect this will make the spin-forbidden transition become allowable. We call the Coulomb integral[24,25]

$$K(a_1 b_1, a_2 b_2) = \langle a_1, b_1 | V_{12} | a_2 b_2 \rangle \quad (20)$$

and the exchange integral

$$J(a_1 b_1, a_2 b_2) = \langle a_1, b_1 | V_{12} | b_2 a_2 \rangle \quad (21)$$

The exchange interaction between the extra electron and the impurity configuration has the following form:

$$H_{ex} = -JS_{Mn}S_e \quad (22)$$

where  $S_{Mn}$  is the total spin of the  $d^5$  configuration in the states of interest,  $S_e$  is spin of the injected electron.  $J$  is the exchange matrix element, which has the form:

$$J_{ii} = \sum_{k,\lambda} \langle \bar{\phi}_k \bar{\phi}_\lambda | V | \phi_\lambda \phi_k \rangle \quad (23)$$

where  $\phi_k$  is the electron wavefunction,  $V$  is the two-electron interaction operator:

$$V(r_1, r_2) = \frac{q_1 q_2}{r_{12}} \quad (24)$$

Because both the wavefunctions of the extra electron and of the  $d^5$  electrons in the  ${}^6A_1$  and  ${}^4T_1$  state are expressed in terms of spherical harmonics, it will be natural that for the two-electron interaction operator  $V$  we will use the expression in terms of the spherical harmonics.  $V$  can be expanded in the form[20]:

$$V(r_1, r_2) = \frac{q_1 q_2}{r_{>}} \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_{<}^k}{r_{>}^k} \sum_m Y_{km}(1) \overline{Y}_{km}(2) \quad (25)$$

If we put the electron functions into equations (20) and (21), the matrix elements will consist of two parts - the radial part and the angular part:

$$\langle \phi_i \phi_j | V | \phi_m \phi_t \rangle = \sum_{k=0}^{\infty} \rho^k(n^i l^i, n^j l^j, n^m l^m, n^t l^t) \times A_k \sigma(s^i s^t) \sigma(s^j s^m) \quad (26)$$

where  $\rho^k(n^i l^i, n^j l^j, n^m l^m, n^t m^t)$  is the radial part

$$\rho^k(n^i l^i, n^j l^j, n^m l^m, n^t m^t) = \langle R_{n^i l^i} R_{n^j l^j} | \frac{e^2 r_{<}^k}{r_{>}^{k+1}} | R_{n^m l^m} R_{n^t l^t} \rangle \quad (27)$$

and  $A_k$  is the angular part

$$A_k = \frac{4\pi}{2k+1} \sum_{p=-k}^{+k} \langle \overline{Y}_{l^i p^i} Y_{kp} Y_{l^t p^t} \rangle \langle \overline{Y}_{l^j p^j} \overline{Y}_{kp} Y_{l^m p^m} \rangle \quad (28)$$

where  $\langle \bar{Y}_{l^i p^i} Y_{k p} Y_{l^t p^t} \rangle$  is a Clebsch-Gordan coefficient, which is different from zero only when the following conditions are satisfied:

$$\begin{aligned} p^i &= p + p^t \\ k + l^i + l^t &= \text{even} \\ l^i - l^t &\leq l^i + l^t \end{aligned} \quad (29)$$

These conditions will reduce the terms in the sum and leave only several matrix elements different from zero.

Now with all the wavefunctions and the interaction form we are ready to calculate the Coulomb and Exchange interaction between the extra electron and the electrons in Mn-center.

#### IV. Exchange Interaction of $Mn^{2+}$ Ion with the Extra Electron in the Nanocrystal

Now we suppose that the extra electron inside the nanocrystal is close enough to the  $Mn^{2+}$  ion at the center so that the electron can couple via exchange interaction with the  $d^5$  electrons in both the ground state  ${}^6A_1$  and the excited state  ${}^4T_1$ . In this section we will consider the effect of this exchange interaction on the impurity electrons in states  ${}^6A_1$  and  ${}^4T_1$ .

The matrix element of the exchange interaction of the extra electron and the impurity electrons in the  ${}^6A_1$  state is:

$$\begin{aligned} &\left\langle {}^6A_1(\vec{r}) \Psi_{1s}^{Dot}(\vec{r}') | V(r - r') | \Psi_{1s}^{Dot}(\vec{r}) {}^6A_1(\vec{r}') \right\rangle \\ &= \left\langle [-\xi^+ \eta^+ \zeta^+ u^+ v^+](r) \varphi_{1s}^{Dot}(r') Y_0^0 | V(r - r') | \varphi_{1s}^{Dot}(r) Y_0^0 [-\xi^+ \eta^+ \zeta^+ u^+ v^+](r) \right\rangle \end{aligned} \quad (30)$$

We should pay attention here to the point that the wavefunction of the  ${}^6A_1$  state of  $d^5$  electrons is a Slater determinant with five single d-electron wavefunctions. So the coordinate  $\vec{r}$  of the  $d^5$  electron wavefunction is actually five different coordinates  $(r_1, r_2, r_3, r_4, r_5)$  of these five single d-electron wavefunctions. In fact, the extra electron has an exchange interaction with each of the five d-electrons. Because these five coordinates are independent, the integrals will be taken separately.

In the calculation of the determinantal matrix elements of (30), we have to deal with the single electron matrix element of the type, for example:

$$\begin{aligned} &\langle \xi(r) \varphi(r') | V(r - r') | \varphi(r) \xi(r') \rangle \\ &= \frac{4\pi q_1 q_2}{j_1(\pi)^2} \frac{1}{R^3} \sum_{k=0}^{\infty} \frac{1}{2k+1} \left\langle \overline{R_{3d}(r)} \sum_{a_i} w_{1S}(r - a_i) \left( \overline{Y_2^1} + \overline{Y_2^{-1}} \right) \overline{j_0} \left( \pi \frac{r'}{R} \right) \overline{Y_0^0} \right| \times \\ &\quad \left. \frac{r^k}{r'^{k+1}} \sum_{m=-k}^k Y_k^m(1) Y_k^m(2) \left| j_0 \left( \pi \frac{r}{R} \right) Y_0^0 R_{3d}(r') \sum_{a'_i} w_{1S}(r' - a'_i) \left( Y_2^1 + Y_2^{-1} \right) \right\rangle \right\rangle \end{aligned} \quad (31)$$

or

$$\begin{aligned}
& \langle \xi(r)\varphi(r')|V(r-r')|\varphi(r)\xi(r')\rangle \\
&= \frac{4\pi q_1 q_2}{j_1(\pi)^2} \frac{1}{R^3} \sum_{k=0}^{\infty} \frac{1}{2k+1} \left\langle \overline{R_{3d}(r)} j_0 \left( \pi \frac{r'}{R} \right) \left| \frac{r^k}{r'^{k+1}} \right| j_0 \left( \pi \frac{r}{R} \right) R_{3d}(r') \right\rangle \\
&\times \left[ \left\langle \overline{Y_2^1 Y_0^0} \left| \sum_{m=-k}^k Y_k^m(1) \overline{Y_k^m}(2) \right| Y_0^0 Y_2^1 \right\rangle \right. \\
&+ \left\langle \overline{Y_2^1 Y_0^0} \left| \sum_{m=-k}^k Y_k^m(1) \overline{Y_k^m}(2) \right| Y_0^0 Y_2^{-1} \right\rangle \\
&+ \left\langle \overline{Y_2^{-1} Y_0^0} \left| \sum_{m=-k}^k Y_k^m(1) \overline{Y_k^m}(2) \right| Y_0^0 Y_2^1 \right\rangle \\
&+ \left. \left\langle \overline{Y_2^{-1} Y_0^0} \left| \sum_{m=-k}^k Y_k^m(1) \overline{Y_k^m}(2) \right| Y_0^0 Y_2^{-1} \right\rangle \right] \sum_{a_i, a'_i} w_{1S}(r - a_i) w_{1S}(r' - a'_i) \quad (32)
\end{aligned}$$

The conditions for non-zero Clebsch-Gordan coefficients give the selection rules for k and m, and also determine the terms of the sum in the radial part. For the exchange interaction k can be only 2. And the radial part of the matrix element becomes:

$$\rho^{Exchange}(3d, s, k = 2) = \int r^2 dr \int r'^2 dr' R_{3d}(r) R_{1s}^{Dot}(r') \frac{r^2}{r'^3} R_{1s}^{Dot}(r) R_{3d}(r') \sum_{a_i, a'_i} w_{1S}(r - a_i) w_{1S}(r' - a'_i) \quad (33)$$

Here  $R_{1s}^{Dot}(r)$  is the envelope function for the electron confined in a dot.  $R_{3d}$  is the orbital function of the 3d-electron, which can be approximately taken as the radial Slater function [20]  $R_{3d}(r) = r^2 e^{-1.87r/a}$ , where  $a = \frac{\hbar^2}{me^2}$ . The sum over the lattice sites will be normalized so as the result we have

$$\rho^{Exchange}(3d, s, k = 2) = \int r^2 dr \int r'^2 dr' R_{3d}(r) R_{1s}^{Dot}(r') \frac{r^2}{r'^3} R_{1s}^{Dot}(r) R_{3d}(r') \quad (34)$$

and for the Coulomb interaction the only possible value of k is 0 and the radial part of the matrix element has the form:

$$\rho^{Coulomb}(3d, s, k = 0) = \int r^2 dr \int r'^2 dr' R_{3d}(r) R_{1s}^{Dot}(r') \frac{1}{r'} R_{3d}(r) R_{1s}^{Dot}(r') \quad (35)$$

The integrals are taken over the dot whose radius is R. Then the radial integral  $\rho(3d, s, k)$  (28) can be computed:

$$\begin{aligned}
\rho^{Coulomb}(3d, s, k = 0) &= \frac{3.96}{R} \\
\rho^{Exchange}(3d, s, k = 2) &= \frac{240[-3(\frac{1.87}{a})^5 \frac{\pi}{R} + 10(\frac{1.87}{a})^3 (\frac{\pi}{R})^3 - 3\frac{1.87}{a} (\frac{\pi}{R})^5]}{[(\frac{1.87}{a})^2 + (\frac{\pi}{R})^2]} \quad (36)
\end{aligned}$$

As the result of the calculation we have for the matrix elements of the Coulomb and Exchange interactions between the extra electron and the  ${}^6A_1$  state:

$$\begin{aligned} K({}^6A_1, {}^1S) &= 5e^2 \rho_{k=0}^{Coulomb} = K, \\ J({}^6A_1, {}^1S) &= \frac{e^2}{25} \rho_{k=2}^{Exchange} = J \end{aligned} \quad (37)$$

And for the Coulomb and Exchange interaction between the extra electron and the  ${}^4T_1$  states:

$$\begin{aligned} K({}^4T_1, {}^1S) &= 5e^2 \rho_{k=0}^{Coulomb} = K, \\ J({}^4T_1xy, {}^1S) &= \frac{e^2}{25} \rho_{k=2}^{Exchange} = J \\ J({}^4T_1z, {}^1S) &= -\frac{e^2}{25} \rho_{k=2}^{Exchange} = -J \end{aligned} \quad (38)$$

And as the effect of the Coulomb and exchange interaction with the injected electron, the levels  ${}^6A_1$  will be shifted and split into 2 sublevels with total spin  $S = 3$  and  $S = 2$  with the corresponding exchange energy:

$$\begin{aligned} E_{ex}({}^6A_1, \varphi(1s, +), S = 3) &= K - \frac{7}{4}J \\ E_{ex}({}^6A_1, \varphi(1s, -), S = 2) &= K + \frac{5}{4}J \end{aligned} \quad (39)$$

with the corresponding wavefunctions:

$$\begin{aligned} |{}^6A_1, \varphi(1s, +), S = 3\rangle &= [-\xi^+ \eta^+ \zeta^+ u^+ v^+] |s+\rangle \\ |{}^6A_1, \varphi(1s, +), S = 2\rangle &= [-\xi^+ \eta^+ \zeta^+ u^+ v^+] |s-\rangle \end{aligned} \quad (40)$$

And the  ${}^4T_1$  levels splits into four sublevels: two sublevels with the value of the total spin  $S = 2$ :

$$\begin{aligned} E_{ex}({}^4T_1, z\varphi(1s, +), S = 2) &= K + \frac{3}{4}J \\ E_{ex}({}^4T_1, xy\varphi(1s, +), S = 2) &= K - \frac{3}{4}J \end{aligned} \quad (41)$$

and the two sublevels with the total spin  $S = 1$

$$\begin{aligned} E_{ex}({}^4T_1, z\varphi(1s, -), S = 1) &= K - \frac{5}{4}J \\ E_{ex}({}^4T_1, xy\varphi(1s, +), S = 2) &= K + \frac{5}{4}J \end{aligned} \quad (42)$$

with the corresponding wavefunctions:

$$\begin{aligned}
|{}^4T_1z, \varphi(1s, +), S = 2 \rangle &= [\xi^+ \eta^+ \zeta^+ \zeta^- u^+] |s+ \rangle + \frac{\beta}{\sqrt{2}} [\xi^2 \eta^+ \zeta^+ p_y^+] |s+ \rangle - \frac{\beta}{\sqrt{2}} [\xi^+ \eta^2 \zeta^+ p_x^+] |s+ \rangle \\
|{}^4T_1xy, \varphi(1s, +), S = 2 \rangle &= \frac{\sqrt{2}}{4} [\xi^+ \xi^- \eta^+ \zeta^+ u^+] |1s+ \rangle + \frac{\sqrt{6}}{4} [\xi^+ \xi^- \eta^+ \zeta^+ v^+] |1s+ \rangle \\
&\quad - \frac{1}{2} [\xi^+ \eta^+ \eta^- \zeta^+ u^+] |1s+ \rangle + [\xi^+ \eta^+ \eta^- \zeta^+ v^+] |1s+ \rangle + \frac{\beta}{2} [\xi^+ \eta^2 \zeta^+ p_z^+] |1s+ \rangle \\
&\quad - \frac{\beta}{2} [\xi^+ \eta^+ \zeta^2 p_y^+] |1s+ \rangle + \frac{\beta}{2} [\xi^2 \eta^+ \zeta^+ p_z^+] |1s+ \rangle - \frac{\beta}{2} [\xi^+ \eta^+ \zeta^2 p_x^+] |1s+ \rangle
\end{aligned} \tag{43}$$

and

$$\begin{aligned}
|{}^4T_1z, \varphi(1s, -), S = 1 \rangle &= [\xi^+ \eta^+ \zeta^+ \zeta^- u^+] |s- \rangle + \frac{\beta}{\sqrt{2}} [\xi^2 \eta^+ \zeta^+ p_y^+] |s- \rangle - \frac{\beta}{\sqrt{2}} [\xi^+ \eta^2 \zeta^+ p_x^+] |s- \rangle \\
|{}^4T_1xy, \varphi(1s, -), S = 1 \rangle &= \frac{\sqrt{2}}{4} [\xi^+ \xi^- \eta^+ \zeta^+ u^+] |1s- \rangle + \frac{\sqrt{6}}{4} [\xi^+ \xi^- \eta^+ \zeta^+ v^+] |1s- \rangle \\
&\quad - \frac{1}{2} [\xi^+ \eta^+ \eta^- \zeta^+ u^+] |1s- \rangle + [\xi^+ \eta^+ \eta^- \zeta^+ v^+] |1s- \rangle + \frac{\beta}{2} [\xi^+ \eta^2 \zeta^+ p_z^+] |1s- \rangle \\
&\quad - \frac{\beta}{2} [\xi^+ \eta^+ \zeta^2 p_y^+] |1s- \rangle + \frac{\beta}{2} [\xi^2 \eta^+ \zeta^+ p_z^+] |1s- \rangle - \frac{\beta}{2} [\xi^+ \eta^+ \zeta^2 p_x^+] |1s- \rangle
\end{aligned} \tag{44}$$

The two sublevels  $|{}^4T_1z, \varphi(1s+), S = 2 \rangle$  and  $|{}^4T_1xy, \varphi(1s+), S = 2 \rangle$  of the  ${}^4T_1$  state of the  $Mn^{2+}$  ion and the sublevel  $|{}^6A_1, \varphi(1s-), S = 2 \rangle$  now have the same total spin  $S = 2$  and the transitions between them now are allowable. In Fig.2 we show the exchange energy splitting of the  ${}^4T_1$  and  ${}^6A_1$  levels and the transitions allowable between them.

So the exchange interaction between the electron injected in the dot and the d- electrons of the Mn-impurity center really make the previously forbidden transition become allowable. In the next section we will give some numerical calculations for the transition probability and the transition lifetime.

## VI. Luminescence and the Lifetime of the Transition

In this section we will give some numerical calculations for the transition probability and the transition lifetime.

The electric dipole transition matrix element between two states  $|i\rangle$  and  $|j\rangle$  is written in the form [23]:

$$\langle i | r \cdot \hat{\epsilon} | j \rangle = \frac{4}{3} \sum_q \left\langle k \left| r \cdot Y_1^q \left( \frac{\vec{r}}{r} \right) \right| s \right\rangle \times Y_1^{-q} \left( \frac{\vec{\epsilon}}{\epsilon} \right) \tag{45}$$

So the matrix element of the transition between the sublevels of the state  ${}^4T_1$  and  ${}^6A_1$  will again have the form of the determinantal matrix element between the wavefunctions (40) and (43). Again, here we can separate the radial and the angular part

$$\begin{aligned} & \left\langle {}^4T_1zz, \varphi_{1s+}^{Dot}, S = 2 |r.\hat{\epsilon}|^6 A_1, \varphi_{1s-}^{Dot} \right\rangle \\ &= \left\langle R_{3d,4p} R_{1s}^{Dot} |r| R_{3d,4p} R_{1s}^{Dot} \right\rangle \langle(i) Y_1^q |(j)\rangle \end{aligned} \quad (46)$$

where  $\langle(i)|r|(j)\rangle$  denote the angular part and the  $\langle|r|\rangle$  – the radial part. Similar to the calculation of the exchange matrix element in the last section, the angular part is calculated using the Clebsch-Gordan coefficients. The radial part also can be computed using the expansion of Bessel function of the dot envelope function  $R_{1S}^{Dot}$ .

Because the interaction with the extra electron relieves the spin forbideness, the transition between the  ${}^4T_1$  and  ${}^6A_1$  states with the same spin  $S = 2$  will be allowed. Note again that the electric dipole transition is allowed due to mixing of the 4p-state into the 3d-states, and depend on the small coefficients  $\beta$ . The matrix element (46) will be based on the one-electron matrix element  $\langle 3d|r|4p \rangle$ , which is allowed with the angular part  $\langle Y_2^l|Y_1^q|Y_2^{l'} \rangle$ . The radial part show a comlicated dependance on the inverse of the dot radius and its powers.

We do some numerical calculations for the case of a quantum dot of Mn- doping ZnS . We use here the standard parameters of Mn and ZnS. For the doped ZnS:Mn quantum dot of radius 50Å, we obtain the splitting due to exchange will be 1.0 to 1.5 eV, which is rather large. The small coefficient  $\beta$  of the parity mixing is reported about  $2.6 - 3^{-2}$ , then the probability of the transition approximately equals  $10^{-3}$ ( the oscillator strength of allowed electric dipole transition has magnitude of 1). It results in a lifetime, that is inversely proportional to the transition probability. The transition lifetime in our calculation is approximately  $2 \times 10^{-5}s$ . The integral strongly inversely depends on the radius of the nanocrystal. For the dot of the radius of 40Å, the transition lifetime is  $1.6 \times 10^{-5}s$ , and it is  $0.9 \times 10^{-5}s$  for the dot of radius 30Å. For a smaller dots, the matrix element will be larger, the probability of the transition will be higher and the transition life-time is shorter.

To compare with the experiments, we notice that our result for the transition lifetime for this size of dot is two orders larger than the transition lifetime in the Mn doped ZnS bulk (1.8 ms). So the presence of an extra electron in the quantum dot really makes the spin-forbidden transition allowable and shortens the life time. The theory supports the results obtained in experimental works [1-4, 8-12] and is close to the result in [10] although we do not obtain the 5 orders of magnitude lifetime shortening, which is reported by R.N. Bhargava et al.[1-4].

### Summary

In this work, we presented a theory for the new model to control the optical transitions in the nanocrystal. By injecting one extra electron into the dot, one can change the transition probability and the optical properties of the nanocrystal. The exchange interaction between the extra electron on the impurity electron splits the energy levels and makes the former spin-forbidden transition become allowable and decreases the lifetime of the transition by about two orders of magnitude.

We are grateful to Dr. Al. L. Efros for his helpful suggestion and discussions and Dr. D. Norris for helpful conversation. We also acknowledge partial support from NYSTAR ECAT Project N°0000067 and PSC-CUNY for this work.

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## FIGURE CAPTIONS

**Fig.1.** Splitting diagram of a single 3d electron in an octahedral crystal field. The five-fold degenerate d-electron with energy  $E_0$  splits in an octahedral crystal field into two levels.

**Fig.2.** Exchange energy splitting of the  $^4T_1$  and  $^6A_1$  states of the  $Mn^{2+}$  ion. Arrows indicate the allowable transitions.